lected and washed with cold THF to give 1.0 g (38% yield based on tripod) of crude **4**. **4** is very soluble in CH_2Cl_2; moderately soluble in benzene, acetone, and toluene; only sparing soluble in THF; and insoluble in nonpolar organic solvents such as pentane or hexane. **4** can be readily recrystallized by slow evaporation from a CH_2Cl_2/C_6H_6/THF mixture. **4** is air-stable in the solid-state for days to weeks, but solutions gradually decompose to unidentified green solutions and should be handled under an inert atmosphere.

Method B. Dissolve $Ni(CO)_2$(tripod) (for literature preparation, see ref 2) in a 50:50 mixture of THF and benzene and let stand in a flask with a rubber septum that has several needle holes punched into it to allow a very slow seepage of oxygen into the flask. Well-formed single crystals of **4** will begin growing from the amber solution after about 2 weeks and will continue to grow until most of the starting material is used up (1-2 months).

Spectroscopic data on $Ni_2(\mu\text{-CO})(CO)_2(dppm)_2$ (**4**): color, yellow; IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 1963 (s, sh), 1942 (vs), 1770 (m); ^1H NMR (ppm, TMS, CH_2Cl_2) 2.6, 3.4 (P-CH_2-P, multiplets, 2 H each), 6.9, 7.0, and 7.3 (Ph, multiplets, 40 H); ^{31}P NMR (ppm, H_3PO_4, CH_2Cl_2) 24.2 (s) (57 to -135 °C); ^{13}C carbonyl NMR (ppm, TMS, 50-80% ^{13}CO enriched, CH_2Cl_2) 200 (s), 243 (quint, J_{P-C} = 7 Hz) (57 to -135 °C). Anal. Calcd for $C_{53}H_{44}Ni_2O_3P_4$ (**4**): C, 64.80; H, 4.52; Ni, 11.66; P, 12.54. Found: C, 64.80; H, 4.52; Ni, 11.66; P, 12.53.

Preparation of $Ni_2(CO)_4(dppm)_2$ (5) and $Ni(CO)_3(dppm)$ (6). Addition of CO to **4** will produce a mixture of **5** and **6**. The ratio of **4**:**5**:**6** is dependent on the temperature and pressure of carbon monoxide. Higher temperatures and lower pressures of CO favor **4**, while the opposite conditions favor species **6**. Crystals of **5** can be grown from CO-saturated CH_2Cl_2 solutions evaporated at 5 °C using a slightly pressurized flow of carbon monoxide. The crystals, however, readily lose both CH_2Cl_2 molecules of crystallization and carbon monoxide at temperatures much above 20 °C. Species **6** has only been observed spectroscopically.

Spectroscopic data on $Ni_2(CO)_4(dppm)_2$ (**5**): color, very pale yellow; IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 2010 (vs), 1995 (vs, sh), 1948 (s, sh), 1933 (vs); ^{31}P NMR (ppm, H_3PO_4, CH_2Cl_2) 19.6 (s) (25 °C); ^{13}C carbonyl NMR (ppm, TMS, 50-80% ^{13}CO enriched, CH_2Cl_2) 196 (s) (25 °C).

Spectroscopic data on $Ni(CO)_3(\eta^1\text{-dppm})$ (**6**): color, colorless; IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 2070 (s), 1995 (vs), 1940 (m); ^{31}P NMR (ppm, H_3PO_4, CH_2Cl_2) doublet-doublet centered at +23.4 and -24.2 (J_{P-P} = 125 Hz).

X-ray Structure Determination on $Ni_2(\mu\text{-CO})(CO)_2(dppm)_2$ (4). Single crystals of **4** were obtained from the NMR tube of $Ni(CO)_2$(tripod) in THF/C_6D_6 after several weeks of standing. A yellow crystal of **4** measuring 0.20 × 0.15 × 0.08 mm was mounted in a glass capillary. Preliminary Weisenberg and precession photographs established the unit cell constants and crystal class (orthorhombic). Data were collected on a Picker FACS-1 computer-controlled diffractometer at room temperature using Mo Kα radiation. Final unit cell constants based on 25 computer-centered reflections are a = 14.015 (2) Å, b = 18.784 (5) Å, c = 22.743 (8) Å, V = 5987 (4) Å^3, and Z = 4.

A total of 3913 reflections were collected and the space group *Pbcn* was uniquely established from systematic absences. The structure was solved by Patterson and direct methods techniques and refined by using 1237 independent reflections with $F_o^2 > 3\sigma(F_o)^2$. The $Ni_2(\mu\text{-CO})(CO)_2(dppm)_2$ molecule sits on a 2-fold crystallographic axis passing through the bridging carbonyl group. There are three solvent molecules of benzene per nickel dimer. The final discrepancy indices are R = 0.062 and R_w = 0.086 with a GOF of 1.19. Crystal parameters, data collection, and structure refinement data are summarized in Table II. A list of fractional coordinates is listed in Table III. Tables of anisotropic thermal parameters and F_o/F_c are included in the supplementary material.

The data to parameter ratio (3.4) is quite a bit smaller than we would like due to the small size of the crystal and the fact that it did not diffract particularly well. There was a monoclinic modification of the crystals that produced much larger crystals, but we were unable to solve the monoclinic structure, even after solving the orthorhombic structure.

Acknowledgment. G.G.S. thanks NATO and CNRS for postdoctoral fellowships and for current NSF funding (Grant CHE-86-13089) allowing extensions of this work to be continued, J.A.O. acknowledges CNRS and GRECO for research funding, and P.H.B. thanks NSERC (Canada) for research support. We also thank Professor Clifford Kubiak (Purdue University) for discussions and copies of his manuscripts prior to publication and Professor Alan Balch (University of California, Davis), who also prepared species **4** at about the same time, for information about his results prior to publication.

Registry No. 1, 75790-05-5; **4**, 106251-27-8; **4**·3C_6H_6, 112965-96-5; **5**, 112896-40-9; **6**, 62945-83-9; $Ni(CO)_4$, 13463-39-3; Ni, 7740-02-0.

Supplementary Material Available: IR spectra of the carbonyl regions for **4**, **5**, and **5**/**6**, tables of thermal parameters, and a full listing of bond distances and angles (5 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Evidence for the Intermediacy of Chromium-Ketene Complexes in the Synthesis of β-Lactams by the Photolytic Reaction of Chromium-Carbene Complexes with Imines. Use in Amino Acid Synthesis

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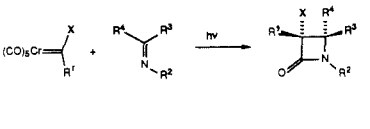
Abstract: Photolysis of chromium-carbene complexes in the presence of nucleophiles gives ketene-derived products. This observation, in conjunction with the stereoselectivity observed in the photolytic reactions of chromium-carbene complexes with imines to produce β-lactams, suggests the intermediacy of photolytically generated, metal-coordinated ketenes. Photolysis of chromium-carbene complexes containing a chiral, optically active amino alcohol group produced lactones in high yield and high diastereoselectivity. These lactones are convertible to optically active amino acids.

A new synthetic approach to β-lactams involving the photolytic reaction of heteroatom-stabilized ("Fischer") chromium-carbene complexes with imines was recently developed in these laboratories (eq 1).[1-4] The process is quite general and tolerates wide variations in the structure of both the carbene and the imine. The reactions proceed in high yield under very mild conditions



(R's = Me, Ph, H; X = MeO, NR_2) (1)

(1) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538.
(2) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

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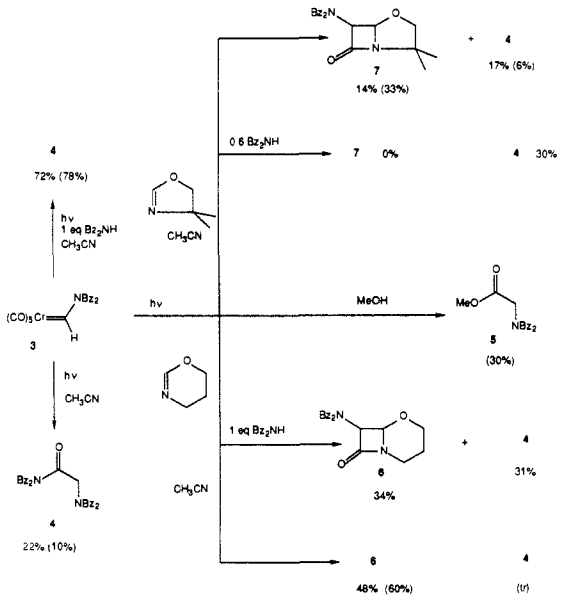
Scheme I[a]



[a] Yields were obtained by integration of characteristic peaks, relative to a standard, in the NMR spectrum. Those in parentheses are for isolated, purified material obtained from a separate preparative-scale experiment.

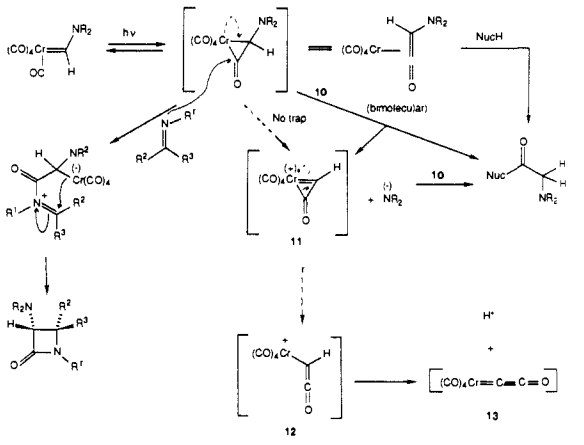
(photolysis in the visible region; THF, Et_2O, or CH_3CN as solvent; 25 °C), and are quite stereoselective, producing a single diastereoisomer in almost all cases. The β-lactam-forming process does *not* occur under thermal conditions, and photolysis at wavelengths of the spectrum, which include the metal-to-ligand charge-transfer absorption[5] (350–450 nm) of the specific carbene complex, is required.

Ketenes were initially considered as reasonable intermediates in this process, since ketenes react with imines to form β-lactams[6] and since metal-carbene complexes have been shown to produce free ketenes under extreme pressures of carbon monoxide[7] or under milder conditions when the carbene complexes are rather unstable.[8] However, the reactions of *free* ketenes with imines suffer from low yields, consumption of ketene by self-condensation (cyclodimerization), and formation of products containing one imine and *two* (or more) ketene fragments. Since these features were absent in the reactions described in eq 1, the intermediacy of free ketenes was dismissed in favor of a pathway involving metallacyclic intermediates commonly invoked (but rarely if ever proven) for thermal reactions of chromium–carbene complexes with olefins and alkynes.[9] However, continuing studies suggest that photolytically generated *chromium–ketene complexes*[10] are important intermediates in the β-lactam-forming reaction (eq 1). Herein, we present evidence supporting this suggestion.

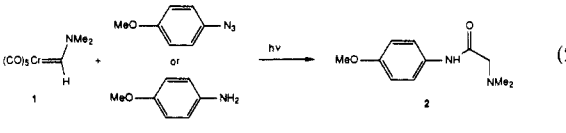
Results and Discussion

The first indication of the formation of chromium–ketene complexes upon irradiation of chromium–carbene complexes came

Scheme II



from unsuccessful attempts to effect a dipolar 1,3-cycloaddition of *p*-methoxyphenyl azide to (dimethylamino)carbene complex **1** (eq 2). Instead of the expected cycloadduct, glycinamide **2** was

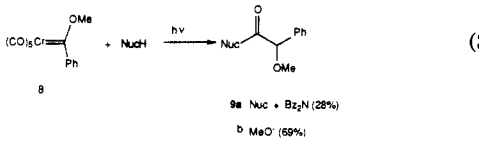


(2)

obtained in ~40% yield. When **1** was irradiated in the presence of *p*-anisidine, >70% yield of **2** was obtained. Similarly, in the reaction of (dibenzylamino)carbene complex **3** with relatively unreactive imines such as oxazolines, tetrabenzylglycinamide derivative **4** was a major byproduct.[3] To clarify and quantify these observations, the reactions in Scheme I were performed. (These reactions were carried out in NMR tubes in CD_3CN and were continuously monitored by ^1H NMR spectroscopy. In most cases the NMR results were confirmed by separate, preparative-scale reactions, with isolation, purification, and characterization of products.)

Photolysis of **3** in the absence of any substrate led to its complete disappearance within 2 h and produced low yields of **4** as the only identifiable organic product. In contrast, repetition of this process in the presence of 1 equiv of dibenzylamine produced high yields of **4**. Irradiation of **3** in methanol produced methyl glycinate **5**. Irradiation of **3** in the presence of 1 equiv *each* of a reactive (toward β-lactam formation) imine (oxazine) and dibenzylamine produced roughly equal amounts of β-lactam **6** and glycinamide **4**, indicating that *reactive* imines and dibenzylamine are similar in their reactivity toward the photogenerated reactive species. In contrast, the same experiment using a relatively unreactive oxazoline as substrate led to exclusive production of **4** and no β-lactam, although low yields of β-lactam **7** are obtained in the absence of added dibenzylamine.

This behavior is not restricted to aminocarbene complexes. Photolysis of methoxyphenylcarbene complex **8** in the presence of methanol or dibenzylamine produced α-methoxyphenylacetic acid derivatives **9a** and **9b** (eq 3). In fact all carbene complexes



(3)

used to produce β-lactams undergo similar reactions with alcohols or amines in the absence of imine substrates. These α-substituted acid derivatives **2**,**4**,**5**, and **9** each consist of the carbene carbon, one carbon monoxide, and the nucleophile. Similarly, the β-lactams previously prepared (as in eq 1) consist of the carbene carbon, one carbon monoxide, and the imine, in this case, the imine. Both classes of compounds are potentially derived by nucleophilic attack on a ketene, yet *free* ketenes or products derived from reactions of free ketenes have never been observed in these reactions. Thus, we are led to a process involving photolytic

(3) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101.
(4) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833.
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(7) Dorrer, B.; Fischer, E. O. *Chem. Ber.* **1974**, *107*, 2683.
(8) Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 874.
(9) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. E. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 783–800.
(10) For a review of metal–ketene complexes, see: Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.*, in press. We thank these authors for providing a preprint of this manuscript.

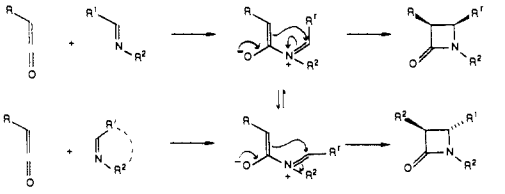
generation of a chromium–ketene *complex* from the chromium–carbene complex and subsequent reaction of this complexed ketene with substrate to produce the observed products. This process is summarized in Scheme II.

The first step involves a photolytically driven insertion of carbon monoxide into the metal–carbon double bond to produce ketene complex **10**. Carbonylation of carbene complexes to produce ketene complexes has previously been observed under CO pressure,[7,8,11] and photolytic insertion of CO into a tungsten–carbon triple bond has recently been reported.[12] Ketene complex **10** appears to be both unstable and reactive. It has not been observed spectroscopically, and its formation is inferred from its subsequent reactions. Two limiting structures for ketene complex **10** are shown. X-ray crystal structures of stable ketene complexes of this type almost invariably have the metallacyclopropanone form rather than the coordinated ketene form.[10] Since the ketene is coordinated, reactions typical of free ketenes, such as dimerization or multiple incorporation in reactions of imines (to give oxazinones[13]), are not observed. In fact, the coordinated ketene is only reactive toward nucleophilic reagents and fails to undergo typical ketene cycloaddition reactions with olefins,[14] such as ethyl vinyl ether or maleic anhydride. Reactions of **10** with nucleophiles such as amines or alcohols produce glycine derivatives, typical ketene-derived products.

Remarkably, in the absence of any substrate or in the presence of relatively unreactive substrates, aminocarbene complex **3** decomposes under photolysis to produce tetrabenzylglycinamide **4**, which contains *two* of the original amino groups, one carbon monoxide, and one carbene carbon. A highly speculative pathway accounting for this is seen in Scheme II. Loss of an amino group from ketene complex **10** (perhaps in a bimolecular transfer of a Bz_2N group between molecules of **10** to give **11** and **4** directly) produces cationic metallacyclopropenone **11**, which rearranges to ketenyl complex **12**. Loss of a proton gives the amino group necessary to react with more of **10** to produce glycinamide as well as metallacumulene **13**. This route is speculative because *none* of the intermediates **10–13** could be spectroscopically detected, and the ultimate fate of **13** is unknown. However, there is ample precedent for complexes such as **11** and **12** in the more stable tungsten series. For example, photolysis of $Cp(CO)_2W{\equiv}CTol$ produced the neutral metallacyclopropenone corresponding to **11**, which rearranged to the stable ketenyl complex equivalent to **12**.[12]

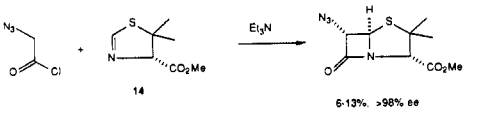
Finally, the photolytic reaction of imines with chromium–carbene complexes is also likely to proceed via metal–ketene complexes. Free ketenes, usually generated in situ from acid halides and triethylamine, react with imines to form β-lactams,[6,15] often with high stereoselectivity. Cyclic imines give pure *trans*-β-lactams, as do imidates and thioimidates. Acyclic imines give mixtures of *cis*- and *trans*-β-lactams, the constitution of which depends on the substituents on the imine and/or on the reaction conditions. The reaction is thought to proceed via a dipolar, nonconcerted pathway, involving nucleophilic attack of the imine on the ketene carbonyl to produce a zwitterionic intermediate, which then undergoes a conrotatory ring closure to form the β-lactam. Mixed stereochemistry results from equilibration of the stereochemistry of the iminium sp^2 carbon in the zwitterion[16] (Scheme III). The low yields of β-lactams often observed in the reaction of free ketenes with imines are due to reaction of the

Scheme III



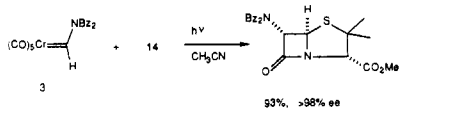
zwitterionic intermediate with more ketene (e.g., to form an oxazinone) rather than with itself to give β-lactam.

The stereochemical outcome of the photolytic reaction of imines with chromium–aminocarbene complexes (eq 1) *exactly parallels* that found with free ketenes, although the yields in the chromium–carbene reaction are much higher. This is best illustrated in the case of chiral thiazoline **14** with which the same *enantioselectivity* is observed with both free azidoketene (eq 4)[17] and



(4)

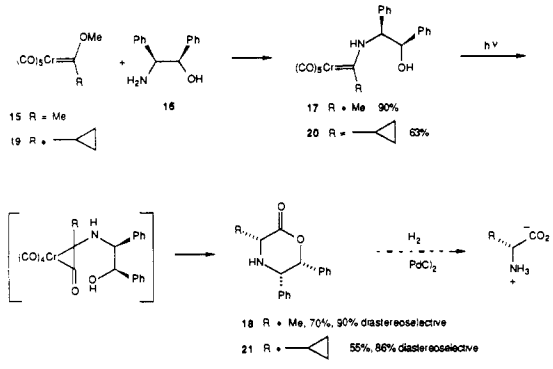
chromium–(dibenzylamino)carbene complex **3** (eq 5).[3] Thus,



(5)

β-lactam formation by nucleophilic attack on the *complexed* ketene, followed by ring closure of the zwitterionic intermediate, is consistent with all of the above observations. Since free ketenes are not present, intermolecular reaction of this *complexed* zwitterionic intermediate with another *complexed* ketene equivalent is not likely, and byproduct formation is not observed, hence the high yields.

The ability to convert chromium–carbene complexes to chromium–ketene complexes, under very mild conditions ($h\nu$, Et_2O, or CH_3CN), and to trap the ketene with nucleophiles has several important synthetic implications. A very large number of differently substituted chromium–carbene complexes are readily available,[18] making unusually substituted coordinated ketenes potentially available for organic synthesis. Since trapping of aminocarbenes with nucleophiles produces α-amino acid derivatives, this provides a potential synthetic route to natural and unnatural amino acids, compounds of considerable recent interest.[19] To determine the feasibility of this, the reactions in eq 6 were



(6)

carried out. Treatment of methoxycarbene complexes **15** or **19** with optically pure D,L-erythro amino alcohol **16**[20] produced aminocarbenes **17** and **20** in good yield. Irradiation (450 W, Pyrex,

(11) Hermann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, J. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* **1984**, *264*, 327.

(12) Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1514.

(13) Martin, J. C.; Brannock, K. C.; Burpitt, R. D.; Gott, P. G.; Hoyle, V. A., Jr. *J. Org. Chem.* **1971**, *36*, 2211. Oxazinones *were* observed in the reaction of the relatively unstable molybdenum carbenes with oxazoline, implying the production of free ketene in these cases; see ref 4.

(14) Brady, R. *Synthesis* **1971**, 415. Luknitskii, V.; Vovsi, L. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 487. For a process that *may* involve intramolecular cycloaddition of an olefin to a coordinated ketene, see: Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461.

(15) Isaacs, N. S. *Chem. Soc. Rev.* **1976**, 181.

(16) Moore, H. W.; Hernandez, L., Jr.; Chambers, R. *J. Am. Chem. Soc.* **1978**, *100*, 2247.

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(18) Dötz, K. H. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983.

(19) For a review, see: Wagner, I.; Musso, H. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 816.

(20) Weijlard, J.; Pfister, K.; Swanezz, E. F.; Robinson, C. A.; Tishler, M. *J. Am. Chem. Soc.* **1951**, *73*, 1216.

18 h, CH_3CN or Et_2O) produced lactones **18** and **21** in fair yield. Diastereoselectivity was estimated by 270-MHz ^1H NMR spectroscopy and HPLC of the crude reaction mixture. The absolute stereochemistry of the major diastereoisomer of **18** was assigned by comparison of its NMR spectrum with that of the same lactone prepared by the recently reported electrophilic glycinate route of Williams.[21] The syn stereochemistry of lactone **21** was assumed by analogy. Since lactones such as **18** are readily cleaved to free amino acids by hydrogenolysis or Li/EtOH reduction, this chemistry should provide a convenient route to α-amino acids. In light of the ease of preparation of carbene complexes having a wide variety of R groups on the carbene carbon (alkyl, aryl, vinyl, cyclopropyl, heteroaromatic), a range of unusual optically active amino acids is potentially available. The results of our efforts in this area will be forthcoming.

Experimental Section

General Procedure. Melting points were taken on a Mel-Temp apparatus and are uncorrected. A Bruker IBM-200 NMR spectrometer was used for the 200-MHz ^1H NMR spectra. The 270-MHz ^1H NMR and the 67-MHz ^{13}C NMR spectra were obtained on a Bruker IBM-270 NMR spectrometer. NMR spectra were recorded in $CDCl_3$, and chemical shifts are given in ppm relative to Me_4Si (0 ppm, ^1H) or $CDCl_3$ (77 ppm, ^{13}C) unless otherwise specified. Assignments in the ^{13}C NMR spectra (broad band) are based on comparison in the measured substance class. IR spectra were recorded on a Beckmann 4240 spectrophotometer. Electron impact (EI) and chemical ionization (CI) mass spectra were obtained on a V. G. Micromass Ltd., Model 16F spectrometer. A Varian Techtron Model 635 or a Perkin-Elmer Lambda 4B UV/Vis spectrophotometer were used for the UV spectra. Optical rotations were obtained on a Perkin-Elmer 24 polarimeter at a wavelength of 589 nm (sodium D line) by a 1.0-dm cell with a total volume of 1 mL. Specific rotation, $[\alpha]_D$, was reported in degrees per decimeter at the specified temperature, and the concentration (c), given in grams per 100 mL in the specified solvent. Ultraviolet irradiation of the reaction mixtures was carried out in 20-mL Pyrex test tubes placed at a distance of 10 cm from a Conrad-Hanovia 7825 medium-pressure mercury lamp operating at 450 W, which was placed in a water-cooled immersion well. A Conrad-Hanovia 7830-C power supply was used.

For the purification of crude reaction mixtures, radial-layer (Chromatotron Model 7924) and column chromatographic techniques were applied in most cases. Merck silica gel 60 PF (for radial-layer chromatography) and Merck silica gel (230–400 mesh) or Alfa activated, neutral aluminum oxide (for column chromatography) were used as stationary phases.

High-performance liquid chromatograms were obtained on a Waters RCM-100 radial compression column (Waters Radial Pak liquid chromatography cartridge, silica gel (8-mm i.d.)) equipped with Model 6000A solvent delivery system and Model R-400 refractive index detector.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Tetrahydrofuran (Fisher, reagent grade) and diethyl ether (ASP, analytical reagent) were predried over CaH_2 and distilled from benzophenone ketyl under a nitrogen atmosphere just prior to use. Hexane (technical grade) was distilled at atmospheric pressure. Ethyl acetate (technical grade) was distilled over CaH_2. Methylene chloride was distilled over CaH_2 or filtered through aluminum oxide (Baker Analyzed, 5 g/100 mL). Acetonitrile (Fisher) was distilled over CaH_2 and stored over 4A molecular sieves. Methanol (Fisher) was dried over Mg and distilled.

Chromium hexacarbonyl (Pressure Chemicals), ethanol (Midwest Solvents, absolute), dibenzylamine (Aldrich), benzene (EM Science), CD_3CN (Sigma, 99% D), p-anisidine (Aldrich), hexamethyldisiloxane (Aldrich), and CaH_2 (Aldrich) were obtained from commercial suppliers and used without further purifications.

The following chemicals were prepared according to the literature procedure: [(*N*,*N*-dibenzylamino)methylene]chromium(0) pentacarbonyl,[3] [(*N*,*N*-dimethylamino)methylene]chromium(0) pentacarbonyl,[3] (phenylmethoxycarbene)pentacarbonylchromium(0), (methylmethoxycarbene)pentacarbonylchromium(0),[22] (cyclopropylmethoxycarbene)pentacarbonylchromium(0),[23] 5,6-dihydro-4*H*-1,3-oxazine,[24] and *d*- and *l*-*erythro*-α,β-diphenyl-β-hydroxyethylamine.[20]

General Procedure for the Synthesis of β-Lactams and Amino Acid Derivatives. Method A. The chromium-carbene complex was placed in a 20-mL Pyrex test tube, which was then sealed with a rubber septum. The vessel was evacuated and purged with argon (three cycles). Dry, degassed acetonitrile or methanol was added via a cannula to produce a 0.02–0.03 M solution of the chromium–carbene complex. The appropriate imine and/or amine was then introduced via a syringe. The solutions were irradiated until most of the carbene had been consumed as judged from analytical TLC (silica gel). After a few minutes of irradiation, the solutions containing aminocarbenes turned from bright yellow to a more intense yellow and were brown at the end of the reaction time. The solutions containing (methoxyphenylcarbene)pentacarbonylchromium(0) were deep red and turned brown. After the irradiation, the solvent was removed under reduced pressure and the residue dissolved in ethyl acetate in an open vessel. Air oxidation of the chromium-containing byproduct(s) was performed in a light box, equipped with six 20-W Vitalite fluorescent lamps. After 1–2 days the solution was clear and contained a dark brown precipitate, which was removed by filtration over Celite. In some cases it proved helpful to filter the reaction mixture one or two times during the oxidation. The clear filtrate was evaporated under reduced pressure and the residue purified by chromatography as described in each synthesis.

Method B. Procedure A was used with the following exceptions. The chromium–carbene complex and the appropriate amine or azide were dissolved in ether or tetrahydrofuran (0.01–0.06 M solution of carbene) in a 20-mL Pyrex test tube, which was then sealed with a rubber septum. The vessel was evacuated and purged with argon (three cycles). The air oxidations were performed by diluting the irradiated samples with a 1:1 mixture of ethyl acetate and hexane.

Photolytic Reaction of [(*N*,*N*-Dimethylamino)methylene]chromium(0) Pentacarbonyl (1) with *p*-Methoxyphenyl Azide. Preparation of Glycinamide 2. The photolytic reaction (method B) of (dimethylamino)carbene complex **1** (100 mg, 0.40 mmol) with p-methoxyphenyl azide (60 mg, 0.40 mmol) in 7 mL of THF for 48 h gave 90 mg of crude product as a brown oil. Purification by preparative TLC (silica gel, 95:5 CH_2Cl_2/MeOH) gave 32 mg (39%) of the product as a yellow oil.

^1H NMR (270 MHz): δ 2.38 (s, 6, $N(CH_3)_2$), 3.07 (s, 2, $CH_2N(CH_3)_2$), 3.80 (s, 3, OCH_3), 6.87 (d, J = 7 Hz, 2, ArH), 7.49 (d, J = 7 Hz, 2, ArH), 9.0 (br, 1, NH). IR (film): 3325 (NH), 1670 (C=O) cm^{-1}. CI MS (NH_3), m/e: 209 (M + 1). Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.46; H, 7.56; N, 13.13.

Photolytic Reaction of 1 with *p*-Anisidine. Preparation of Glycinamide 2. The photolytic reaction (method B) of (dimethylamino)carbene complex **1** (249 mg, 1.00 mmol) with p-anisidine (123 mg, 1.00 mmol) in 20 mL of THF for 26 h gave 140 mg (67%) of the product as a yellow oil. This compound was identical (IR, NMR) with that reported above.

Photolysis of (Dibenzylamino)carbene Complex 3 in CH_3CN. A test tube containing **3** (72 mg, 0.179 mmol) in 10 mL of CH_3CN (0.02 M solution) was prepared as described under method A, irradiated for 4 h, and air-oxidized for 20 h. Column chromatography (silica gel, 230–400 mesh, benzene/ethyl acetate 30:1 to 10:1) of the crude reaction mixture (25 mg) gave 4 mg (9 μmol; 10%) of tetrabenzylglycinamide **4** as a colorless oil.

Photolysis of 3 in the Presence of Dibenzylamine. A test tube containing **3** (32 mg, 80 μmol) and dibenzylamine (17 μL, 88 μmol) in 3 mL of CH_3CN (0.03 M solution of **3**) was prepared as described under method A, irradiated for 5 h and air-oxidized for 24 h. Radial-layer chromatography (silica gel, hexane/ethyl acetate 4:1) of the crude reaction mixture (34 mg) gave 27 mg (62 μmol; 78%) of **4** as a colorless oil.

^1H NMR (270 MHz): δ 3.35 (s, 2, $COCH_2N$), 3.76 (s, 4, two amine NCH_2), 4.32 (s, 2, amide NCH_2), 4.56 (s, 2, amide NCH_2), 6.85 (m, 2, ArH), 7.15–7.31 (m, 18, ArH). ^{13}C NMR (67 MHz): δ 171.1(CO), 138.7, 137.3, 136.6, 129.2, 128.5, 128.2, 127.2, 127.1, 126.4 (ArC), 58.4 (two amine NCH_2), 55.3 ($COCH_2$), 49.3 and 47.9 (two amide NCH_2). IR (CCl_4): 3080, 3060, 3030, 1648 (CO), 1492, 1450, 1425, 688 cm^{-1}. EI MS, m/e (relative intensity): 343 (13, $M^+ - 91$), 210 (29), 106 (66), 105 (72), 103 (100), 91 (91), 77 (73). CI MS (NH_3): m/e 434 (M^+). Anal. Calcd for $C_{30}H_{30}N_2O$: C, 82.90; H, 6.97; N, 6.45. Found: C, 82.87; H, 6.78; N, 6.41.

Photolysis of 3 in Methanol. A test tube containing **3** (100 mg, 249 μmol) in 15 mL of methanol (0.02 M solution) was prepared as described under method A, irradiated 10.5 h, and air-oxidized for 46 h. Column chromatography (silica gel, 230–400 mesh, benzene) of the crude reaction mixture (57 mg) yielded 20 mg (74 μmol, 30%) of methyl glycinate **5** as a colorless oil.

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^{1}H NMR (200 MHz): δ 3.30 (s, 2, $COCH_2$), 3.67 (s, 3, OCH_3), 3.80 (s, 4, two NCH_2), 7.20–7.40 (m, 10, ArH). ^{13}C NMR (67 MHz): δ 171.8 (CO), 139.1, 128.9, 128.3, 127.1 (ArC), 57.9 (two NCH_2), 53.5, 51.0 ($COCH_2$ and OCH_3). IR (CCl_4): 3080, 3060, 3020, 1750 (sh), 1735 (CO), 1490, 1450, 1430, 1185, 1168, 1145, 685 cm^{-1}. EI MS, *m/e* (relative intensity): 269 (1, M^+), 210 (35), 106 (32), 105 (37), 103 (31), 91 (100), 77 (44). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.80; H, 7.12; N, 5.20. Found: C, 75.68; H, 7.04; N, 5.07.

Photolysis of [(*N*,*N*-Dibenzylamino)methylene]chromium(0) Pentacarbonyl (3) in the Presence of 5,6-Dihydro-4*H*-1,3-oxazine. A test tube containing **3** (51 mg, 127 μmol) and oxazine (11 mg, 129 μmol) in 6 mL of CH_3CN (0.02 M solution) was prepared as described under method A, irradiated for 4 h, and air-oxidized for 14 h. Column chromatography (silica gel, 230–400 mesh, benzene/ethyl acetate 7:1) of the crude reaction mixture (37 mg) gave 26 mg (76 μmol, 60%) of oxacepham **6**.[3]

Photolysis of [(*N*,*N*-Dibenzylamino)methylene]chromium(0) Pentacarbonyl (3) in the Presence of 4,4-Dimethyl-1,3-oxazoline. A test tube containing **3** (51 mg, 127 μmol) and oxazoline (13 mg, 131 μmol) in 6 mL of CH_3CN (0.02 M solution) was prepared as described under method A, irradiated for 4 h, and air-oxidized for 14 h. Column chromatography (silica gel, 230–400 mesh, methylene chloride/ethyl acetate 40:1) of the crude reaction mixture (30 mg) gave 14 mg (42 μmol, 33%) of β-lactam **7**[3] and 3 mg (7 μmol, 6%) of tetrabenzylglycinate **4**.

NMR Experiments. Preparation of Samples for the Irradiation in NMR Tubes. Method A. The solution of carbene **3** (10 mg, 0.025 mmol) in CD_3CN was filtered through a small amount of Al_2O_3 into an NMR tube, which was constantly flushed with a stream of argon. The other reactants as well as hexamethyldisiloxane (internal standard for the integration) were introduced via syringe. The sample was then degassed by five thawing–freezing cycles (0.05 mmHg; dry ice/isopropyl alcohol), and the NMR tube was sealed under argon with a regular NMR cap. The disappearance of starting material(s) and the appearance of product(s) were carefuly monitored by integration over appropriate signals in the NMR spectra during irradiation. The integration was judged to be accurate to ±5% at the beginning and ±10% toward the end of the photolysis. The relative amounts of starting materials were measured by integration at $t = 0$.

Method B. The reactants were introduced into the NMR tube as described under method A, but these samples were not degassed by the thawing–freezing technique.

Photolysis of Methoxyphenylcarbene 8 in Methanol. A test tube containing **8** (100 mg, 320 μmol) in 13 mL of methanol (0.03 M solution) was prepared as described under method A, irradiated for 15 h, and air-oxidized for 25 h. Column chromatography (silica gel, 230–400 mesh, benzene/ethyl acetate 30:1) of the crude reaction mixture (50 mg) gave 40 mg (222 μmol, 69%) of methoxy ester **9b**[25] as a colorless oil.

^{1}H NMR (270 MHz): δ 3.41 (s, 3, OCH_3), 3.72 (s, 3, $COOCH_3$), 4.78 (s, 1, CH), 7.35–7.46 (m, 5, ArH). ^{13}C NMR (67 MHz): δ 171.0 (CO), 136.3, 128.6, 128.5, 127.2 (ArC), 82.7 (CH), 57.3, 52.0 (OCH_3 and $COOCH_3$). IR (CCl_4): 3090, 3060, 3030, 2840 (OCH_3), 1755 (CO), 1740 (sh), 1490, 1450, 1430, 1190, 1165, 1105, 1005, 685 cm^{-1}. EI MS, *m/e* (relative intensity): 180 (1, M^+), 121 (100), 105 (40), 91 (31), 77 (68).

Photolysis of 8 in the Presence of Dibenzylamine. A test tube containing **8** (80 mg, 256 μmol) and dibenzylamine (50 μL, 260 μmol) in 14 mL of CH_3CN (0.02 M solution of **8**) was prepared according to method A, irradiated for 14 h, and air-oxidized for 36 h. Column chromatography (silica gel, 230–400 mesh, benzene/ethyl acetate 6:1) of the crude reaction mixture (56 mg) gave 25 mg (72 μmol, 28%) of **9a** as a colorless oil.

^{1}H NMR (200 MHz): δ 3.43 (s, 3, OCH_3), 4.39 (AB system, 2, J = 15 Hz, δ_A 4.32, δ_B 4.46, CH_2N), 4.56 (AB system, 2, J = 15 Hz, δ_A 4.32, δ_B 4.80, CH_2N), 5.07 (s, 1, CH), 6.95–6.99 (m, 2), 7.09–7.13 (m, 2), 7.23–7.48 (m, 11, ArH). ^{13}C NMR (67 MHz): δ 170.6 (CO), 136.6, 128.7, 128.4, 127.4, 127.1, 126.9 (ArC), 83.5 (CH), 57.7 (OCH_3), 49.1, 48.2 (two NCH_2). IR (CCl_4): 3080, 3060, 3030, 2820 (OCH_3), 1660, 1640 (CO), 1490, 1450, 1420, 1100, 685 cm^{-1}. EI MS, *m/e* (relative intensity): 345 (0.5, M^+), 254 (1), 224 (9), 194 (2), 121 (48), 106 (30), 105 (41), 103 (45), 91 (100), 77 (43). Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.96; H, 6.72; N, 4.06. Found: C, 80.12; H, 6.77; N, 4.16.

Synthesis of Aminocarbene 17. Chromium–carbene **15** (533 mg, 2.13 mmol) and amino alcohol **16** (454 mg, 2.13 mmol) were dissolved in 15 mL of absolute ethanol. The reaction vessel was evacuated and purged with argon (three cycles) to replace the air with argon. Stirring was continued at room temperature for 24 h. The solvent was removed in vacuo, and the yellow residue was purified by column chromatography (alumina, CH_2Cl_2) to give aminocarbene **17** (826 mg, 90%) as a yellow oil, which crystallized upon sitting: mp (hexane) 106–107 °C; $[\alpha]^{25}_D$ −144.6° (*c* 5.16, CH_2Cl_2).

^{1}H NMR (270 MHz): δ 2.31 (d, J = 3 Hz, 1, OH), 2.49 (s, 3, CH_3), 5.00 (dd, J = 4 and 8 Hz, 1, CH), 5.22 (t, J = 4 Hz, 1, CH), 6.95 (m, 2, ArH), 7.05 (m, 2, ArH), 7.30 (m, 6, ArH), 9.7 (br, 1, NH). IR (film): 3580 (OH), 3350 (NH), 2030 (s, CO), 1990–1850 (CO) cm^{-1}. UV (hexane): λ_{max} 365 nm (ε 3400 M^{-1} cm^{-1}). Anal. Calcd for $C_{21}H_{17}NO_6Cr$: C, 58.47; H, 3.97; N, 3.25. Found: C, 58.36; H, 4.01; N, 3.28. EI MS, *m/e* (relative intensity): 431 (0.3, M^+), 347 (0.3), 319 (0.4), 180 (75), 179 (80), 178 (57), 103 (100).

Synthesis of Aminocarbene 20. This was prepared according to the procedure given above for aminocarbene **17**, except that the reaction time was increased to 2 weeks. Chromium–carbene **19** (471 mg, 1.71 mmol) and amino alcohol **16** (421 mg, 1.98 mmol) in 5:1 THF/EtOH were stirred until no chromium–carbene **19** was visible by TLC (silica gel, CH_2Cl_2). Isolation as above gave 494 mg (63%) of the desired product as a yellow oil.

^{1}H NMR (270 MHz, $CDCl_3$): δ 0.75 (m, 1, cyclopropyl CH_2), 1.10 (m, 3, cyclopropyl CH_2), 1.67 (m, 1, cyclopropyl CH), 2.30 (s, 1, OH), 5.20 (s, br, 2, 2C*H*Ph), 6.90 (m, 2, ArH), 7.05 (m, 2, ArH), 7.30 (m, 6, ArH), 9.65 (s, br, 1, NH). IR (film): 3580 (OH), 3360 (NH), 2040 (CO), 2000–1860 (s, CO) cm^{-1}. UV (hexane): λ_{max} 370 nm (ε 5300 M^{-1} cm^{-1}. Anal. Calcd for $C_{23}H_{19}NO_6Cr$: C, 60.40; H, 4.19; N, 3.06. Found: C, 60.29; H, 4.38; N, 2.99.

Photolysis of Aminocarbene 17. Preparation of Lactone 18. A test tube containing aminocarbene **17** (105 mg, 0.240 mmol) and 15 mL of acetonitrile was prepared as described in method A, irradiated 24 h, and air-oxidized for 18 h to give 54 mg (84%) of lactone **18** as the major product. The diastereoselectivity of the reaction was determined to be 90% by ^{1}H NMR integration and 88% by HPLC (5:1 hexane/ethyl acetate). Radial-layer chromatography (neutral alumina; hexane, 5:1 hexane/CH_2Cl_2) of the crude reaction mixture gave 45 mg (70%) of lactone **18** as a white solid.

***anti*-18.** ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.59 (d, J = 7 Hz, 3, CH_3), 1.67 (s, br, 1, NH), 4.13 (q, J = 7 Hz, 1, C*H*CH_3), 4.73 (d, J = 4 Hz, 1, NC*H*Ph), 5.73 (d, J = 4 Hz, 1, OC*H*Ph), 6.8–7.4 (m, 10, ArH).

***syn*-18.** ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.61 (d, J = 7 Hz, 3, CH_3), 1.75 (s, br, 1, NH), 4.06 (q, J = 7 Hz, 1, C*H*CH_3), 4.66 (d, J = 4 Hz, 1, NC*H*Ph), 5.62 (d, J = 4 Hz, 1, OC*H*Ph), 6.80 (m, 2, ArH), 6.90 (m, 2, ArH), 7.25 (m, 6, ArH). IR (KBr): 3320 (s, NH), 1725 (s, C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.11; H, 6.25; N, 5.20.

Photolysis of Aminocarbene 20. Preparation of Lactone 21. A test tube containing aminocarbene **20** (43 mg, 0.094 mmol) in 10 mL of diethyl ether was prepared according to method B, irradiated 12 h, and air-oxidized for 18 h to give 21 mg of crude lactone **21** as a colorless oil. The diastereoselectivity of the reaction was determined to be 86% by ^{1}H NMR integration and 84% by HPLC (5:1 hexane/ethyl acetate). Purification by column chromatography (Merck silica gel 60 silianized, 70–230 mesh; hexane, 2:1 hexane/CH_2Cl_2) gave 15 mg (55%) of lactone **21** as a colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$): δ 0.35 (m, 1, cyclopropyl CH_2), 0.65 (m, 2, cyclopropyl CH_2), 0.85 (m, 1, cyclopropyl CH_2), 1.45 (m, 1, cyclopropyl CH), 1.8 (s, br, 1, NH), 3.28 (d, J = 8 Hz, 1, NC*H*(C_3H_5)), 4.62 (d, J = 4 Hz, 1, NC*H*Ph), 5.55 (d, J = 4 Hz, 1, OC*H*Ph), 6.80 (m, 2, ArH), 6.90 (m, 2, ArH), 7.25 (m, 6, ArH). IR (film): 3310 (NH), 1740 (C=O) cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.70; H, 6.34; N, 4.72.

The cyclopropyl signals for the minor (anti) diastereoisomer in the ^{1}H NMR spectrum were unassignable. The methines appeared at δ 3.40 (d, J = 8 Hz, 1, NC*H*(C_3H_5)), 4.83 (d, J = 4 Hz, 1, NC*H*Ph), and 5.68 (d, J = 4 Hz, 1, OC*H*Ph).

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Supplementary Material Available: Listing of experimental data for NMR experiments described in Scheme I (3 pages). Ordering information is given on any current masthead page.

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